



Letter to the Editor

Comment on “Designed oxygen carriers from macroporous LaFeO₃ supported CeO₂ for chemical-looping reforming of methane”, by Zheng et al. [Appl. Catal. B: Environ., 202 (2017) 51–63. doi: 10.1016/j.apcatb.2016.08.024]



In a recent article, Zheng et al. studied catalytic systems involving CeO₂ nano-particles (2–3 nm in size), which are finely dispersed over the wall surface of a three-dimensional ordered macro-porous LaFeO₃ substrate, for use in the method of oxygen carrier-assisted Chemical Looping Reforming of Methane (CLRM) [1]. The authors recall that: “La-based perovskite-type oxides, such as LaFeO₃, are known to contain large concentrations of vacancies in their structure, reversibly pick up and deliver oxygen at high temperatures.” They also recall that: “CeO₂ is one of the most attractive... materials that have a high oxygen storage capacity due to its ability to release/acquire oxygen through redox processes involving the Ce⁴⁺/Ce³⁺ couple”. The authors aim to show that combining ceria with LaFeO₃ substantially improves the yield of the CLRM process, and they explain it as a function of the catalyst's intimate structure and chemistry. To accomplish this, they conduct scanning electron microscopy, transmission electron microscopy, x ray diffraction, and x ray photoelectron spectroscopy (XPS) analyses, as well as H₂-temperature programmed reduction (TPR) tests, and CH₄-TPR and CH₄-temperature programmed desorption (TPD) tests. From these experiments, they derive an interpretation, which in their view explain the catalytic properties of these materials [1].

Here, I shall comment on the authors' interpretation of their XPS spectra, specifically Ce3d, Fe2p, and O1s spectra of x%CeO₂/LaFeO₃ (x = 5, 10, 20 wt%) samples as a function of x and of CLRM cycling. Though XPS is just one of the diagnostic tools the authors used in their study, it has the unique potential to throw some light on two aspects that are crucially important to the scope and aims of their article. Firstly, XPS maps the chemistry of the cerium and it measures the atomic ratio of the Ce⁴⁺/Ce³⁺ redox couple [2,3], two findings that directly relate the oxygen carrier properties of ceria to the performance of the catalyst. Secondly, it probes just the outermost region of materials, i.e. the first 2–5 nm, and this allows one to access the surface chemistry of cerium, iron and oxygen ions resulting from the interactions of the ceria with both the LaFeO₃ substrate and the surroundings. While I find that Zheng et al. achieve and document some important progress in the catalytic performance of these materials [1], I believe that a good part of their interpretation of XPS results is unwarranted. XPS Ce3d spectra of Ce³⁺ and Ce⁴⁺ oxides involve an unusual peak multiplicity, which arises from two sources. The first is the strong electron–electron correlation of Ce4f and O2p orbitals in both the initial state and, especially, in the final state [4–7], which produces two peaks in the Ce3d spectrum. In order of increasing binding energy (BE) the first and second peaks arise from the bonding state and anti-bonding state both of which involve admixtures of Ce4f¹ and Ce4f² configurations, respectively, for both Ce³⁺ and Ce⁴⁺ oxide ions. Moreover, the non-hybridized, pure Ce4f⁰ configuration contributes a third peak, which falls on the high-BE region of the Ce⁴⁺ oxide spectrum [7]. Thus, while XPS spectra of most elements of the Periodic Table have one peak only for each spin orbit component [8,9], Ce⁴⁺ and Ce³⁺ oxidic species produce, respectively, three peaks and two peaks in each of them.

The second sort of peak multiplicity depends on spin orbit interaction, which is of general occurrence not only in Ce3d spectra, but also to spectra of all chemical elements originating from a core-hole in an electronic level with $l \neq 0$. Spin orbit interaction doubles the number of peaks over the two Ce3d ($l = 2$) components, giving a total of six peaks in the spectrum of Ce⁴⁺ oxide and four in that of Ce³⁺ oxide [10]. Moreover, in Ce3d spectra of cerium oxides both the mutual BE separations between, as well the mutual intensities of, the peaks produced by Ce⁴⁺ and Ce³⁺ ions have constant, well precise values. Theoretical studies [6,7] derived the coefficients of the hybridization-induced admixed Ce4f¹ and Ce4f² configurations (as well as of the non-hybridized configuration Ce4f⁰ of the Ce⁴⁺ ion) that best reproduce the mutual energy separations and intensities of Ce3d peaks of experimental spectra in each of the two spin orbit split components [11–16]. Furthermore, j - j interaction ($j = l \pm s = l \pm \frac{1}{2}$) of 3d electrons ($l = 2$) dictates that the spin orbit separation, ΔE_{so} , of each pair of corresponding Ce 3d peaks is a constant for each cerium ion ($\Delta E_{so} = 18.4 \pm 0.2$ eV for Ce³⁺, and $\Delta E_{so} = 18.5 \pm 0.2$ eV for Ce⁴⁺ [14]) and that constant also is their intensity ratio. Indeed, given that $j +/ - = 2 \pm \frac{1}{2}$, two j values are obtained, 5/2 and 3/2, whose populations $N_{ji} = 2ji + 1$, are: $N_{j+} = 2 \times 5/2 + 1 = 6$, and $N_{j-} = 2 \times 3/2 + 1 = 4$ [10,17]. As a result, their ratio comes to the constant value of $N_{j+}/N_{j-} = 6/4 = 1.50$ [14].

To recapitulate, each oxidic cerium ion produces three (Ce⁴⁺-related) and two (Ce³⁺-related) Ce3d peaks as a result of electron correlation, which are doubled over the two (5/2;3/2) components of the 3d level as a result of spin orbit interaction, giving a total of six and four peaks in the Ce3d spectrum, respectively. Moreover both the BE separations and relative intensities within the peak sets of the two components Ce3d5/2 and Ce3d3/2 have well defined, constant values, which are a function of the electron correlation phenomena relevant to the specific cerium ion (that is, whether Ce³⁺ or Ce⁴⁺). Furthermore, constant also are the BE separations and the intensity ratios between the pairs of corresponding peaks distributed over the two Ce3d components owing, respectively, to spin-orbit interaction, as well as to the branching ratio of electron population relevant to the two 3d spin orbit components.

It is just by meeting all these requisites, which underlie the ‘architecture’ of Ce3d spectra involving Ce⁴⁺ and Ce³⁺ ions, that can one locate the peaks specifically relevant to them and derive through them the atomic ratio of the two ions. Indeed the coexistence of the two ions produce as many as ten peaks, which are packed up in a BE interval of ~ 40 eV (~ 880 to 920 eV). In particular some of them lie so close to each other, that peak-fitting procedures are the only way to resolve Ce3d spectra as the combination of a Ce⁴⁺-related ‘sextet’ with a Ce³⁺-related ‘quartet’. In other words, one ought to use the same requisites as constraints of one's peak fitting [14,16]. Moreover, some of the interrelationships between the spectral parameters of the two ions should be further tested in comparison Ce3d spectra recorded, with the same spectrometer, on surfaces of pure CeO₂ and

Ce₂O₃ before using them as constraints to peak-fit the ceria-bearing samples under investigation [14,16].

Identification and quantification of iron and oxygen ions are comparatively easy to bring about in XPS Fe2p and O1s spectra, respectively. In the Fe2p spectrum ($l = 1$), a given iron species has a single peak, which in the case of paramagnetic ions is broadened to the high-BE side by a series of close-lying peaks in each component ($j = 2 \pm \frac{1}{2} \rightarrow 3/2; 1/2$). Given that the electron populations of the two spin orbit split peaks are such that: $N_{3/2} = 2 \times 3/2 + 1 = 4$ and $N_{1/2} = 2 \times 1/2 + 1 = 2$, their intensity ratio comes to a constant value of $4/2 = 2$. O1s spectra are even easier to handle, because a given oxygen species produces a single peak, with no spin orbit splitting ($l = 0$).

In view of all this, I would point out the following.

According to Zheng et al.'s peak fittings of the Ce3d spectra in Fig. 3 of their article both Ce⁴⁺ species and Ce³⁺ species are present in both samples 10%Ce₂O₃/LaFeO₃ and 20%Ce₂O₃/LaFeO₃. I argue that:

(i) The authors largely ignore the aforementioned requisites governing the number, the energy separations and mutual intensities of 3d electrons for both Ce³⁺ and Ce⁴⁺ ions. Moreover, they do not test these quantities in comparison spectra on the two cerium oxides recorded separately, and with the same experimental conditions as those adopted for the Ce3d spectra of their catalysts.

(ii) The authors' claim that these materials contain sizable amounts of Ce³⁺ oxidic species is untenable.

Addressing point (ii) first, I note that the authors assume in their peak fittings that it is just peaks \dot{V} (Ce3d5/2) and \dot{U} (Ce3d3/2) that bear witness to the presence of Ce³⁺ oxidic species, whereas they omit the corresponding spin orbit split companion peaks V⁰ and U⁰ at BEs of 880.6 and 898.9 eV, respectively [14]. In other words, although a Ce3d spectrum produced by the coexistence of Ce⁴⁺ and Ce³⁺ oxidic species contains ten peaks, the authors assume that it contains only eight. As Zheng et al. ignore the findings available in the primary XPS studies of cerium oxides [3,6,7,13–16], they base their interpretation on the results reported in an article by Si et al., dealing with CeO₂-ZrO₂ systems, according to which the Ce3d spectrum of materials that involve the two cerium ions “can be decomposed into eight components” [18]. (Oddly enough, the latter authors [18] cite, as Ref [25], of their bibliography, the article by Pfau and Schierbaum, which is one of the primary XPS studies of cerium oxides [16], but their interpretation is at variance with its finding and recommendations on how one should peak fit complex Ce3d spectra.) Unfortunately, to ‘obliterate’ peaks V⁰ and U⁰ in the peak fitting of Ce3d spectra of cerium oxides has become a very popular practice in the literature [19–22]. The main (if not only) aim of such a practice seems to be the attainment of the best match of the peak-fitting with the experimental Ce3d spectrum even at the cost of selecting Ce3d peaks on the basis of empirical criteria, and not of the XPS theoretical/experimental primary literature of cerium oxides. Indeed the peak fittings that Zheng et al. report in Fig. 3 of their article are two such cases [1]. I also note that Ce3d spectra involving the Ce³⁺/Ce⁴⁺ atomic ratios measured by the authors ought to show both the emergence of the Ce³⁺-related peak \dot{V} in the “valley” between peaks V and \dot{V} and a broadening to the low BE side of (Ce⁴⁺-related) peak V, owing to the emergence of (Ce³⁺-related) peak V⁰ [2,12,14]. Neither of these two spectral features is visible in Ce3d spectra reported by the authors in Fig. 3. Also, reference studies [2,14] have acknowledged that it may be difficult to account for the presence and measure the intensity of peak V⁰ (and U⁰) in Ce3d spectra produced by surfaces containing low amounts of Ce³⁺ species, approximating perhaps to 5–10% of the total cerium content [2,14], but not for the percentages which Zheng et al. measured in their materials. In view of all this, I argue that their materials contain no appreciable amounts of Ce³⁺ species, especially not those relevant to the Ce³⁺/Ce⁴⁺ atomic ratios reported in Table 1 of their paper.

To address point (i), I shall refer to the BE values, listed in Table 1 of the present article, which I derived from the two Ce3d spectra reported by the authors in Fig. 3 of their article. Though the Ce3d spectra in Fig. 3 have a relatively low intensity and signal-to-noise ratio, one can reasonably assume that it is possible to measure their peak BEs with an uncertainty of ± 0.3 eV, a task which I accomplished in previous ‘readings’ of published peak-fittings of Ce3d spectra recorded on cerium oxide systems [23]. As can be seen in Table 1 of the present article, the BE values of peak \dot{V} differ by 1.3 eV (10%CeO₂/LaFeO₃) and 1.5 eV (20%CeO₂/LaFeO₃) from the reference value [14]. Such differences are strikingly high, and in particular they are far higher than the uncertainty associated with my ‘reading’ of the graphs in Fig. 3, considering that the authors used an XPS instrument equipped with a monochromatized AlK α source [1].

Though the Ce3d spectra shown by Zhu et al. [24] (Ref [27], in Zheng et al.'s bibliography) contain neither peak V⁰ nor peak U⁰, yet the presence of peak \dot{V} does visibly emerge in the valley between peaks V and \dot{V} at BE = 885.9 eV, a value which differs by only 0.1 eV from the reference value [14]. Even in the article by Si et al. [25], which Zheng et al. use as Ref [50], in their article, the presence of trivalent cerium is marked by peaks \dot{V} and \dot{U} , which fill up the “valley” regions between peaks V and \dot{V} and U and \dot{U} , respectively (again, neither peaks V⁰ and U⁰ are marked in the spectra but the authors refer to them in parentheses as being embedded in the foot of peaks V and U, respectively [25]). Accurate peak fittings of Ce3d spectra involving Ce³⁺/Ce⁴⁺ atomic ratios comparable with those obtained by Zheng et al., reported the sharp emergence of peak \dot{V} in the “valley” between peaks V and \dot{V} , as well as a visible broadening to the low BE side of (Ce⁴⁺-related) peak V, owing to the presence of (Ce³⁺-related) peak V⁰ [2,12,14]. Neither of these two spectral features is visible in the two Ce3d spectra of Fig. 3, and their absence leaves the authors' claim regarding the occurrence of Ce³⁺ species in their catalysts [1] undemonstrated. What is even more remarkable, the Ce⁴⁺-related fitting peak \dot{V} marked in the spectrum of sample 10%CeO₂/LaFeO₃, lies at a BE value which is ~ 2.4 eV higher than the reference value [14]. This BE shift does not depend on the interaction of ceria with LaFeO₃, that is, it is not a chemical shift depending on the change of the chemical environment/coordination of the Ce⁴⁺ ion. In fact the spin orbit corresponding peak \dot{U} lies at a BE value which differs by only 0.3 eV from the expected value. Put another way, had the BE shift of peak \dot{V} been caused by the chemical interaction with LaFeO₃, peak \dot{U} , too, would have shifted by the same extent, given that the aforementioned quantity ΔE_{so} for Ce⁴⁺-related Ce3d peaks is a constant value within ± 0.2 experimental uncertainty [14]. This suggests that some of the BEs the authors obtained in their Ce3d spectra are flawed not only by the aforementioned inaccuracy problems – hardly compatible with XPS spectra obtained with a monochromatized AlK α source – but also by precision/reproducibility problems (more of this later).

Table 1

The BE values (in electron-volts) which I derived, with an estimated uncertainty of ± 0.3 eV, at the peak maxima of the peak fittings of Ce3d spectra reported by Zheng et al. [1] in Fig. 3. For the sake of simplicity, the nomenclature 10%CeO₂ and 20%CeO₂ denote samples 10%CeO₂/LaFeO₃ and 20%CeO₂/LaFeO₃, respectively. The last two rows list reference Ce3d BEs of cerium oxides. (*) From Ref. [14].

Sample	V ⁰	V	V'	V''	V'''	U ⁰	U	U'	U''	U'''
10%CeO ₂	–	882.5	884.1	891.2	898.2	–	900.8	903.3	908.3	916.4
20%CeO ₂	–	882.5	883.9	888.9	898.2	–	900.8	903.4	907.8	916.5
CeO ₂ *		882.6		888.8	898.4		901.0		907.4	916.7
Ce ₂ O ₃ *	880.6		885.4			898.9		904.0		

Since the Ce3d spectra in the article by Zheng et al. are displayed with rather small dimensions, a fact that makes it hard to accurately measure the intensity of the fitting peaks, I did not attempt a systematic quantitative analysis of the two spectra of Fig. 3. I just note that, as far as the spectrum of sample 10%CeO₂/LaFeO₃ is concerned, one can reasonably assume that peak V has about the same intensity as that of the spin orbit split, corresponding peak U. One can also assume that the intensity of peak \hat{V} is even lower than that of peak \hat{U} , while the theoretical intensity ratio for all pairs of spin orbit corresponding Ce3d peaks, I_V^1/I_U^1 , is always 1.50 [10].

Moreover, given that the authors in their peak fittings totally omit both peaks V⁰ and U⁰, the intensity of each of which accounts for more than one third of the total Ce³⁺-related peak intensity ($I_V^0/I_V^1 = I_U^0/I_U^1 = 0.55$ [10]), the same peak fittings underestimate the actual abundance of this cerium ion accordingly. Unfortunately, the authors do not show the Ce3d spectrum or the O1 s spectrum of the pure ceria sample which they prepared and used in their catalysts to check what the chemical state of one of their starting ingredients was like, and in particular, how its spectra compared with those of the CeO₂/LaFeO₃ catalysts.

Though the authors say that their Fe2p spectrum of LaFeO₃ in Fig. 3 involves trivalent iron, and that both its BE values and lineshape compare well with those reported in the article by Tirumalairajan et al. [26], (listed as Ref [49]. in their bibliography), this is not actually the case. For one thing, the Fe2p_{3/2} peak recorded by Tirumalairajan et al. has a smooth lineshape, if broadened to the high BE side [26] – as also other XPS studies of LaFeO₃ have reported [27–30], whereas the Fe2p_{3/2} component Zheng et al. recorded on that material has a structured profile, see Fig. 3a. The authors fitted it with two peaks lying at 712.5 and 714.9 eV, and the BE of the latter, which has the dominating intensity, is at sharp variance with the results of XPS studies of LaFeO₃ [26–30]. Before I discuss possible explanations for the presence of this XPS signal and its ‘high’ BE value, I note that its structured lineshape is not a consequence of the interaction of ceria with LaFeO₃, because it is clearly visible only in the Fe2p spectrum of pure LaFeO₃, see Fig. 3a. I also note that such a lineshape, in fact, differs from those of the Fe2p spectra of the other three samples of Fig. 3, although the authors keep marking the occurrence of the ‘high’ BE Fe2p_{3/2} peak even in those three spectra. To my mind, there are not 2 discrete Fe³⁺-related peaks in the BE region ~712–715 eV of the latter three Fe2p spectra, but just a broadening to the high BE side of the Fe2p_{3/2} peak at 712.5 [1]. Such broadening is due to a series of close-lying components, none of which, incidentally, induces a discrete structure to the profile of the Fe2p_{3/2} lineshape. These arise from the exchange interaction between the unpaired electron left after Fe2p_{3/2} photoemission and the unpaired electrons in the Fe3d orbital of the Fe³⁺ ion [31,32], as well as from shake up satellites [32,33]. To associate a Fe2p_{3/2} BE value of 714.9 with a Fe³⁺ ion is quite problematic. In fact, a Fe2p_{3/2} BE ~715 eV peak has never been reported in XPS studies of either LaFeO₃ [26–30] or iron oxides and hydroxides [32,34–37]. Moreover its value is hardly compatible with even the BEs measured on trivalent iron, unless it derives from compounds such as the following: Fe₂(SO₄)₃(NH₄)₂SO₄·24H₂O (iron(III) sulfate ammonium sulfate hydrate) [38] or FeF₃, iron fluoride [39,40]. It might also derive from the presence of foreign material such as tin metal (XPS Sn3p_{3/2} peak) [41], or be in fact the Auger signal of some Co-bearing species (the Auger CoL₂₃M₂₃V transition may well produce peaks at a kinetic energy value of ~772.0 eV, which corresponds to a BE value ~1487–772 ~ 715 eV when AlK α radiation is used as a source) [42]. Another possibility is that the ‘high’ BE Fe2p_{3/2} peak is in fact the manifestation of differential charging and/or electron-induced chemical modifications of the sample being irradiated by the electron gun [43]. Interestingly, the BE shift between the ‘high’ BE peak and the ‘regular’ Fe2p_{3/2} peak is 2.4 eV, that is, the same shift that I discussed above for the unusually high BE value of peak \hat{V} in the Ce3d spectrum of sample 10%CeO₂/LaFeO₃. Though I did not attempt to analyze the peak-fitted Fe2p spectra of Fig. 3 quantitatively, mere visual inspection suggests that the Fe2p_{3/2} intensity ratio between the Fe²⁺-related peak and the corresponding Fe³⁺-related peaks of both spectra 3b and 3d is higher than that of spectrum 3c, despite the authors’ observation that just the converse is the case. Unfortunately, the authors did not record general, wide-scan general XPS spectra in the BE range of, say, 0–1000 eV, which would have assisted in ascertaining whether the occurrence of the aforementioned high-BE Fe2p_{3/2} peak was in fact due to a foreign chemical species. The authors find that a high-BE Fe2p_{3/2} peak is present also in the Fe2p spectra which they recorded on LaFeO₃ and sample 10%CeO₂/LaFeO₃ after subjecting them to 30 CLRM cycles, see Fig. 12. I note that, on a rough estimate, the BE values of both the two Fe³⁺-related Fe2p_{3/2} peaks that Zheng et al. mark in their peak fittings are ~ 1.5 eV lower than those they obtained before the cycling treatment, whereas the corresponding BE of the Fe²⁺-related Fe2p_{3/2} varies only by ~ 0.5 eV. Unfortunately, the authors reported neither Ce3d nor O1 s spectra of CLRM cycled pure ceria nor those of CLRM cycled 10%CeO₂/LaFeO₃.

I also note that the authors in the Fe2p spectra of Figs. 3 and 12 peak fitted only the Fe2p_{3/2} component and not the Fe2p_{1/2} one, for which one expects the same spectral features as those of the Fe2p_{3/2}, though scaled by a 1/1.50 = 0.67 factor [10]. Now, it seems that the Fe²⁺-related peak could be indeed accommodated also in the Fe2p_{1/2} companion component of the three spectra of Fig. 3 where it occurs. By way of contrast, the ‘high’ BE Fe2p_{3/2} peak has no analogous structured peak in the companion Fe2p_{1/2} component which apparently features a continuous, smooth lineshape. Such spectral difference is contrary to the correspondence criterion between the two spin orbit components of XPS peaks dictated by theory [10].

This further leads one to exclude the source of this ‘high’ BE Fe2p_{3/2} peak from being the LaFeO₃ CeO₂ interaction; it suggests, rather, that the aforementioned hypotheses of the presence of surface contamination or instrumental artifacts are more probable reasons for the presence of the ‘high’ BE Fe2p_{3/2} peak.

Concerning their O1s spectra shown in Fig. 3, the authors say “Generally, the oxygen defect concentration over the CeO₂-based materials is proportional to the O_{ads}/O_{latt} ratio. The relatively higher O_{ads}/O_{latt} ratios over the 10%CeO₂/LaFeO₃ and 5%CeO₂/LaFeO₃ samples than the pure LaFeO₃ indicates that adding suitable amount of CeO₂ could enhance the formation of oxygen defects. This must be related to the chemical interaction between CeO₂ and LaFeO₃. For the 20%CeO₂/LaFeO₃ sample, the relatively low oxygen defect concentration should be attributed to the agglomeration of CeO₂ particles on the material (as observed by TEM measurement)” [1]. In other words, Zheng et al. hold that the intensity of the high-BE O1s components scale with ceria-related oxygen vacancies. They apparently assume that the alleged occurrence of Ce³⁺ oxidic species produces the increase of high-BE O1s signals in their Ce3d spectra. However, the high-BE O1s components, i.e., components lying at BEs higher than that produced by lattice oxygen, may arise from several other sources, since the authors’ samples experienced prolonged exposure to the laboratory atmosphere and as such they developed and/or adsorbed at the surface carbonates as well as hydroxo-species, such as water, hydrates and so on [44]. Since all these species also occur on the surface of cerium oxides [45] (as we have seen, Zheng et al. report no XPS O1s spectra of their ceria sample), combination of the latter with LaFeO₃ obviously increases the relative intensity of the aforementioned high-BE components in the O1s spectra of samples 10%CeO₂/LaFeO₃ and 20%CeO₂/LaFeO₃. In other words, this increase is not of necessity due to the CeO₂-LaFeO₃ interaction, because it might as well occur with any other material, including those with no oxygen vacancy, whose surface is rich in hydrated/carbonated species. As a result, there are good reasons to believe that the increase in the high-BE O1s component is the result of a cumulative hydration effect, rather than an oxygen-vacancy-related effect, as the authors seem to imply [1]. Zheng et al. also say that the XPS spectra “were registered after purging the samples at ambient temperature under vacuum (residual pressure < 10^{−7} Pa)” [1]. Room temperature ‘purging’ is not *per se* sufficient either to free the samples’ surface of adsorbed hydrates, or to fill up oxygen vacancies of ceria. Indeed, Mullins et al. [46] find that “The O 1s peak at

533.5 eV (i.e., one of the high-BE components) is not related to the presence of either Ce^{3+} or Ce^{4+} ions but of OH^- species, and that it can be “removed by annealing the samples to 600–700 K.” Thus, surface hydrated contamination can be removed only when cerium oxide is annealed at those high temperatures, and not just the room temperature at which the authors ‘purged’ their samples [1]. Elsewhere, Mullins and co-workers [47] do find that the adsorption of water occurs either on virtually stoichiometric CeO_2 , or defective CeO_2 , but that the intensity of the high BE O1s component relative to that produced by lattice oxygen ions is considerably lower than that which Zheng et al. show in Fig. 3. These studies [46,47] also find that, again, the key factors ruling the oxidation state and extent of ceria surfaces, defective or otherwise, are the temperature at which water is adsorbed onto the two surfaces, and the temperature at which the latter are subsequently annealed. Other studies [2,16] find that the O1s spectrum of defective ceria surfaces develops an additional, high-BE component lying at ~ 2.5 eV above that of lattice oxygen but, again, its intensity is only ca. 5–8% as great as that of lattice oxygen [16]. There is every reason to believe that LaFeO_3 is in fact the main source of both the high-BE O1s components produced by adsorbed water, hydrates and carbonates, as well as of the component at ~ 529 eV due to lattice oxygen in Fig. 3 and Fig. 12. Indeed, LaFeO_3 is the host material of the catalysts that Zheng et al. analyzed (that is, its content is far superior to ceria’s) [1], and even in pure LaFeO_3 , that is, in the absence of ceria, the O1s spectra in Fig. 3 and Fig. 12 show the dominating presence of the high-BE components at ~ 532 and ~ 534 eV. Note also that the O1s spectra of LaFeO_3 are produced by surfaces that involve no appreciable amount of oxygen vacancy because no Fe^{2+} -related component is found in the corresponding Fe2p spectra, see Fig. 3a and Fig. 12a [1].

In sum, I argue that the XPS results presented by the authors show that in these $\text{CeO}_2/\text{LaFeO}_3$ catalysts there are Fe^{2+} species, but actually no appreciable amount of Ce^{3+} oxidic species. One might object that the absence of Ce^{3+} -related signals in the Ce3d spectra of Fig. 3 is due to the oxidation of Ce^{3+} species to Ce^{4+} species, as a result of their exposure to ambient oxygen. My response is that such objection conflicts with the evidence offered in some detailed surface science studies of stoichiometric ceria and defective ceria. Henderson et al. [2] showed that Ce^{3+} oxidic species are the result of “substantial reduction of the first layer along with some subsurface reduction that was not re-oxidized by RT exposure to O_2 .” Pfau and Schierbaum similarly say that the oxidation treatment “at room temperature with O_2 does not restore the stoichiometry (of defective ceria surfaces) even at high exposures,” but this could be only achieved by oxidizing the surface at $T = 523$ K [16]. Moreover, in pioneering XPS studies Barr [45] did demonstrate that the natural passivation layer of cerium metal surfaces have Ce_2O_3 -like species as the most abundant constituent of cerium metal at RT, and that those species do not oxidize to CeO_2 at that temperature. Bear in mind that Zheng et al. kept the samples inside the vacuum of the XPS spectrometer in an attempt to “purge” them, and all of their spectra were recorded on surfaces that were invariably and constantly kept at room temperature.

Furthermore, XPS O1s results by Thirumalairajan et al. [26] showed that LaFeO_3 is highly hygroscopic, and I think this is one of the main reasons for the O1s spectra in Fig. 3. Other reasons are that ceria is less hygroscopic than LaFeO_3 , and that the extent of such hygroscopicity scales with its dispersion of CeO_2 nanoparticles over the wall of LaFeO_3 , that is, with their ability to spread their moisture upon the formation of $x\%\text{CeO}_2/\text{LaFeO}_3$ materials. Indeed, samples 5% $\text{CeO}_2/\text{LaFeO}_3$ and 10% $\text{CeO}_2/\text{LaFeO}_3$, which feature a comparatively high dispersion of ceria particles [1] (see Fig. 1c1 and c2 and Fig. 1e1 and e2, respectively), produce $I_{(\text{OI}+\text{OII})}/I_{(\text{OIII})}$ intensity ratios (Fig. 3 (b), (c) and Table 1), which are substantially higher than that observed in the spectrum of LaFeO_3 (Fig. 3a and Table 1). Conversely, sample 20% $\text{CeO}_2/\text{LaFeO}_3$, which features a comparatively compact distribution of agglomerated ceria particles [1] (see Fig. 1d1 and d2), produces an $I_{(\text{OI}+\text{OII})}/I_{(\text{OIII})}$ intensity ratio (Fig. 3d and Table 1) which is even lower than that which the authors measured on pure LaFeO_3 . Again, the O1s spectrum of pure ceria would have been useful to reveal the hydration degree present in one of the starting materials from which the authors prepared their samples.

The $I_{(\text{OI}+\text{OII})}/I_{(\text{OIII})}$ intensity ratios obtained for LaFeO_3 and 10% $\text{CeO}_2/\text{LaFeO}_3$, which were subjected to 30 CLRM redox cycles prior to XPS analysis, are both lower than those measured on the non-cycled samples, see Fig. 12 and Table 2. As can be seen, the ratio for 10% $\text{CeO}_2/\text{LaFeO}_3$ is slightly higher than that of LaFeO_3 [1]. These results suggest that the CLRM cycling treatment has in some ways removed a good part of oxygen-bearing adsorbed species off the surfaces of the two samples [1], including those contributed by the addition of ceria. If we recall that through XRD analysis the authors observed that “the effect of redox treatment on the crystal structure of 10% $\text{CeO}_2/\text{LaFeO}_3$ sample is not significant” [1], we can assume that neither the dispersion of ceria nanoparticle was affected with respect to that of non-cycled 10% $\text{CeO}_2/\text{LaFeO}_3$.

To conclude, while I acknowledge that Zheng et al. designed $\text{CeO}_2/\text{LaFeO}_3$ materials that feature an outstanding CLRM performance, their XPS results present some problems in point of accuracy, reproducibility, methodology and completeness. A specific problem with completeness is that the authors limited their quantitative analysis to atomic ratios or atomic percentages involving chemical species of the same element [1], such as $[\text{Ce}^{3+}]/[\text{Ce}^{4+}]$, $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$ and $\{[\text{O}_I] + [\text{O}_{II}]\}/[\text{O}_{III}]$, respectively (Table 1 and Table 2), but they did not derive atomic ratios such as $[\text{Ce}]/[\text{Fe}]$ and/or $[\text{Ce}]/[\text{La}]$ etc. by which they could have monitored how the surface elemental composition of a given sample compared with its nominal value.

Thus, despite the unique diagnostic potential of the XPS technique, these results offer little or no information about the chemical interaction of CeO_2 with LaFeO_3 and the attendant oxygen storage/release properties of the catalysts resulting from their combination. A consequence of this is that the said XPS results cannot substantiate and corroborate the reaction mechanism that the authors propose to explain the catalytic performance of their materials [1], nor do they in themselves and by themselves offer a basis to any alternative reaction mechanism.

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